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(51) Int. Cl.^{3}:	Classification Symbols:	Internal Office Registration Nos.:
C 01 B 33/32	101	6765-4G
33/24		6765-4G

No. of Inventions: 1 (Total of 13 pages)

Examination Request: Not requested

(54) Method for manufacturing calcium sodium silicate hydrate

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[There are no amendments to this patent.]

Specifications

1. Title of the invention

Method for manufacturing calcium sodium silicate hydrate

2. Claims

1 A method for manufacturing calcium sodium silicate hydrate, characterized by the fact that a suspension containing a sodium component, a silicon dioxide component and a calcium

component is reacted hydrothermally under pressurization in such a way that the raw material charging coefficient (T) and the alkalinity coefficient (U) calculated using equations (A) and (C), when a sodium salt is by-produced by the reaction, and calculated using equations (B) and (D) when no sodium salt is by-produced by the reaction are in the range of 1.2-3.0 and larger than 0.01, respectively, with the amounts of Na_2O, SiO_2, CaO and H_2O in the suspension taken as X mol, Y mol, Z mol and S mol, respectively.

$$T = 9Y-32Z/9X-12Z \dots (A)$$
$$T = 9Y-32Z/9X-3Z \dots (B)$$
$$U = 3X-4Z/3S \dots (C)$$
$$U = 3X-Z/3S \dots (D)$$

(where the numerators and denominators in equations (A)-(D) are all positive numbers).

2. The method described in Claim 1, characterized by the fact that the temperature of the hydrothermal reaction is 150-250°C.

3. The method described in Claim 1, characterized by the fact that the silicon dioxide component and the sodium component are sodium silicate.

4. The method described in Claim 1, characterized by the fact that the silicon dioxide component is hydrous silicic acid or clay.

5. The method described in Claim 1, characterized by the fact that the sodium component is sodium hydroxide.

6. The method described in Claim 1, characterized by the fact that the calcium component is calcium hydroxide or calcium oxide.

7. The method described in Claim 1, characterized by the fact that the calcium component is at least one compound selected from the group of calcium chloride, calcium nitrate and calcium sulfate.

3. Detailed explanation of the invention

The present invention pertains to a method for manufacturing calcium sodium silicate hydrate.

More specifically, the present invention provides a method for manufacturing a special calcium sodium silicate hydrate by carrying out a hydrothermal reaction for a reaction system in which a sodium component, a silicon dioxide component and a calcium component exist under special conditions.

Silicate salts exist in many compounds as natural substances, but only a very limited number of silicate salts are chemically synthesized. The present inventors have performed extensive research on manufacturing silicate salts by means of a hydrothermal synthesis reaction

As a result of this research work, the present inventors have succeeded in synthesizing the well-known pectolite as a natural substance or the novel calcium sodium silicate hydrate. The present invention was achieved based on the aforementioned research work.

The present invention provides a method for manufacturing calcium sodium silicate hydrate, characterized by the fact that a suspension containing a sodium component, a silicon dioxide component and a calcium component is reacted hydrothermally under pressurization in such a way that the raw material charging coefficient (T) and the alkalinity coefficient (U) calculated using equations (A) and (C), when a sodium salt is by-produced by the reaction, and calculated using equations (B) and (D) when no sodium salt is by-produced by the reaction are in the range of 1.2-3.0 and larger than 0.01, respectively, with the amounts of Na_2O, SiO_2, CaO and H_2O in the suspension taken as X mol, Y mol, Z mol and S mol, respectively.

$$T = 9Y-32Z/9X-12Z \ldots (A)$$
$$T = 9Y-32Z/9X-3Z \ldots (B)$$
$$U = 3X-4Z/3S \ldots (C)$$
$$U = 3X-Z/3S \ldots (D)$$

(where the numerators and denominators in equations (A)-(D) are all positive numbers).

There are two types of novel calcium sodium silicate hydrates obtained in the present invention. Both are crystalline and have intrinsic diffraction lines under powder X-ray diffraction.

One of the calcium sodium silicate hydrates has strong diffraction lines at spacing $d(\text{Å}) = 12.0, 6.0, 3.4$ and 3.0 (the calcium sodium silicate hydrate having the aforementioned characteristics of X-ray diffraction is simply referred to as the 12 Å type hereinafter). The other calcium sodium silicate hydrate has strong diffraction lines at spacing $d(\text{Å}) = 13.4, 6.7$ and 3.1 (the calcium sodium silicate hydrate having the aforementioned characteristics of X-ray diffraction is simply referred to as the 13 Å type hereinafter). The 13 Å type of calcium sodium silicate hydrate usually also has strong diffraction lines at $d(\text{Å}) = 3.5, 3.3, 3.0$ and 2.9. The two types of calcium sodium silicate hydrates can both be represented by the general formula $lK_2O \cdot mNa_2O \cdot 4CaO \cdot 15-17SiO_2 \cdot nH_2O$ (where, $l \geq 0$, $m \geq 0$, $4 \geq l+m > 0$, $n > 0$). However, the values of l and m vary depending on the crystal type, that is the 12 Å type or 13 Å type, and on the manufacturing conditions, etc. The pectolite obtained in the present invention is a well-known compound that exists in nature. Its general formula is $NaCa_2Si_3O_8(OH)$.

In the following, a typical method for manufacturing the calcium sodium silicate of the present invention will be explained in detail. However, the method for manufacturing the calcium sodium silicate of the present invention is not limited to the one to be explained in the following. The manufacturing method should be modified appropriately as demanded.

As can be seen from the chemical formulas of the aforementioned three types of calcium

sodium silicate hydrates, the raw materials used in the present invention require at least three components, that is a silicon dioxide component, a calcium component and a sodium component. The materials used for supplying these three components can be selected independently for each component. It is also possible to select a single compound that can supply at least two components. In other words, there is no special limitation on the raw materials used for supplying the aforementioned components as long as a silicon dioxide component, a calcium component and a sodium component exist in the solution of the reaction system. In general, it is preferred to use the following raw materials. Examples of the preferred raw materials of the silicon dioxide component include hydrous silicic acid, which is usually called white carbon, that is silicon dioxide manufactured using the dipping method, clay, quartz, and other types of silicon dioxide or compounds containing silicon dioxide. As to be explained later, however, it is also particularly preferred to use sodium silicate as the raw material for the silicon dioxide. In industry, it is usually preferred to use sodium hydroxide as the raw material for the aforementioned sodium component. It is also preferred to use the aforementioned sodium silicate in industry. Sodium silicate is a particularly preferred raw material in industry because, when it is used as the raw material in the present invention, it can be used as the raw material for both the aforementioned silicon dioxide component and the sodium component. There is no special limitation on the raw material used for the aforementioned calcium component as long as it is water soluble under the conditions of the hydrothermal reaction carried out under pressurization. In general, examples of the preferred raw materials used for the calcium component include calcium hydroxide, calcium oxide, calcium chloride, calcium nitrate, calcium sulfate and other water-soluble calcium compounds. Water solubility means that the raw material used for the calcium component can be dissolved in water in the aforementioned reaction system. For example, said calcium sulfate cannot be well dissolved when the raw materials are mixed. However, since it can provide enough dissolved calcium needed for the calcium sodium silicate generated during the reaction, it is still possible to use calcium sulfate as a raw material in the present invention. Nevertheless, it is undesirable to use calcium carbonate or other calcium compound that is hard to dissolve as a raw material in industry because these compounds have a very low reaction speed and will take several days to react, depending on the reaction conditions. Similarly, when calcium chloride, calcium nitrate or other calcium salt is used as the raw material, they will react with the aforementioned sodium component to form sodium chloride, sodium nitrate, sodium sulfate or other by-product. Sometimes, these by-products can be separated from the calcium sodium silicate of the present invention, depending on their solubilities. However, they become undesirable raw materials when it is necessary to completely remove a small amount of by-products. On the other hand, when calcium hydroxide or calcium oxide is used as the calcium compound, the aforementioned by-

product is usually not generated. Consequently, calcium hydroxide and calcium oxide are the best raw materials for the calcium component as far as avoiding mixing of the by-products is concerned.

In the present invention, there is no special limitation on the sequence of adding the aforementioned raw materials. The raw materials can be added simultaneously or separately into an aqueous medium. It is also possible to add the various raw materials into different aqueous media, then mix the obtained aqueous solutions or suspensions. Regardless of the method that is adopted, the aqueous medium in which the silicon dioxide component, sodium component and calcium component are mixed is usually in the form of a suspension. There is no special limitation on the concentrations of the raw materials in the aqueous medium. The concentrations of the raw materials can be selected appropriately as long as the hydrothermal reaction can be carried out. In general, in order to manufacture the calcium sodium silicate hydrate efficiently in industry, the concentrations of the silicon dioxide component and the sodium component are usually higher than that of the calcium component in the reaction system. More specifically, the conditions suitable for efficiently manufacturing the calcium sodium silicate hydrate of the present invention in industry will be explained in the following.

When the raw materials are added into an aqueous medium, a suspension is usually obtained as described above. In the present invention, it is most preferred that the raw material be added in such amounts that the following conditions are satisfied. In other words, the amounts of the raw materials added should be determined in such a way that the raw material charging coefficient (T) and the alkalinity coefficient (U) calculated using equations (A) and (C), when a sodium salt is by-produced by the reaction, and calculated using equations (B) and (D) when no sodium salt is by-produced by the reaction are in the range of 1.2-3.0 and larger than 0.01, respectively, with the amounts of Na_2O, SiO_2, CaO and H_2O in the suspension taken as X mol, Y mol, Z mol and S mol, respectively.

$$T = 9Y\text{-}32Z/9X\text{-}12Z \text{ ... (A)}$$
$$T = 9Y\text{-}32Z/9X\text{-}3Z \text{ ... (B)}$$
$$U = 3X\text{-}4Z/3S \text{ ... (C)}$$
$$U = 3X\text{-}Z/3S \text{ ... (D)}$$

(where the numerators and denominators in equations (A)-(D) are all positive numbers).

As explained above, the generation of a sodium salt as a by-product of the reaction is mainly caused by the use of a calcium salt, such as calcium chloride, calcium sulfate or calcium nitrate. If no sodium salt is generated as a by-product of the aforementioned reaction, it means that either calcium hydroxide or calcium oxide is used as the calcium component.

At present, the effects of the aforementioned raw material charging coefficient (T) and alkalinity coefficient (U) on the reaction for generating the calcium sodium silicate hydrate are

still not clear. The equations used for calculating the aforementioned raw material charging coefficient (T) are derived by the present inventors from many experimental results. If this coefficient has a value smaller than the aforementioned lower limit, the reaction for generating the calcium sodium silicate hydrate might take as long as several days or even tens of days, which is considered a disadvantage in industry. On the other hand, if the coefficient (T) is larger than the aforementioned upper limit, a large amount of amorphous silica or quartz will be by-produced or left over, and it is difficult to separate them from the targeted product, that is the calcium sodium silicate hydrate. This is undesirable because mixing of the impurities becomes inevitable. To obtain the calcium sodium silicate hydrate of the present invention alone, it is usually preferred to select a raw material charging coefficient (T) of 2.5 or smaller although the specific value may vary slightly depending on the types of raw materials and the reaction conditions. Consequently, the raw material charging coefficient (T) that is used most frequently in industry is in the range of 1.2-2.5. The targeted calcium sodium silicate hydrate of the present invention can be obtained even if the aforementioned alkalinity coefficient (U) is 0.01 or smaller. In the present invention, however, the alkalinity coefficient (U) should have a value larger than 0.01. Nevertheless, if the alkalinity coefficient (U) is too large, there will be a lot of unreacted sodium component. As a result, the device cannot be operated efficiently. Also, the unreacted sodium component will cause problems in the reaction cycle. Therefore, a value of 0.04 or smaller is desired for practical applications.

The preferred standards for the relationships of the raw material charging coefficient (T) and alkalinity coefficient (U) have been explained in the above. The optimum values, however, vary depending on the types of raw materials, reaction conditions, etc., and cannot be determined univocally. Consequently, in practical applications, the preferred values should be determined depending on the types of raw materials, reaction conditions, etc., in advance.

In the following, several examples of the methods for determining the aforementioned raw material charging proportions will be explained. In the present invention, almost the entire amount of the calcium component is consumed for generating the calcium sodium silicate hydrate when the reaction is carried out with the raw material charging coefficient (T) and alkalinity coefficient (U) in the desired ranges. In other words, if the amount of the calcium sodium silicate hydrate to be generated is determined, the required molar amount of CaO (said Z mol) in the suspension can be determined. The molar ratio of H_2O/CaO is then determined appropriately. The molar ratio of H_2O/CaO determines the concentration of the solid matter in the suspension and should be selected appropriately in the range of 100-600 based on the relationship with the volume of the device in which the hydrothermal reaction is carried out. If the molar ratio of H_2O/CaO is lower than 100, the viscosity of the suspension becomes too high during the hydrothermal reaction. As a result, part of the suspension might be solidified. On the

other hand, if the molar ratio is higher than 600, the volume of the device required becomes too large with respect to the amount of the generated calcium sodium silicate. If the molar ratio of H_2O/CaO is determined, the molar amount of H_2O (said S mol) can be determined. The value of the alkalinity coefficient (U) is then determined appropriately. If it is assumed that the alkalinity coefficient (U) is set at 0.03, the required molar amount of Na_2O can be determined. Finally, the molar amount of SiO_2 is determined in an appropriate manner so that (T) calculated from the equation of the raw material charging coefficient (T) lies in the aforementioned preferred range.

When sodium silicate is used as the silicon dioxide component and the sodium component, the raw material charging proportions can be determined as follows. In general, for sodium silicate, the molar ratio of SiO_2/Na_2O is in the range of 1.0-3.5. In other words, it is easy to start using sodium metasilicate No. 4 as the raw material. The molar ratio of SiO_2/Na_2O is usually determined beforehand depending on the availability, cost, etc., of the sodium silicate used as the raw material. In this case, the molar amount of SiO_2 (said Y mol) and the molar amount of Na_2O (said X mol) can be determined corresponding to the amount of the sodium silicate used. After the raw material for the calcium component is determined, it is possible to determine which equation, that is said equation (A) or (B), should be used to calculate the raw material charging coefficient (T). The molar amount of CaO in the aforementioned suspension should be determined appropriately so that the raw material charging coefficient (T) is in the range of 1.2-3.0. Also, the molar amount of H_2O (said S mol) should be determined appropriately so that the molar ratio of H_2O/CaO is in the range of 100-600, and the alkalinity coefficient (U) is larger than 0.01. Also, when sodium silicate is used as a raw material, the molar amount of CaO can be first determined corresponding to the amount of the calcium sodium silicate to be generated as described above. The molar ratio of H_2O/CaO is then determined from the molar amount of CaO, and the molar ratio SiO_2/Na_2O of the sodium silicate is determined from the relationship involving the aforementioned alkalinity coefficient (U) or the relationship involving the aforementioned raw material charging coefficient (T).

The calcium sodium silicate hydrate obtained in the present invention can be classified into fibrous pectolite, two types of mica-shaped crystalline calcium sodium silicate, two types of mica-shaped amorphous silica containing calcium sodium silicate, or their mixture. The reasons for generating said fibrous pectolite, absence/presence of amorphous silica in the calcium sodium silicate, or generating the 12 Å type or 13 Å type mica-shaped compound are still not clear. According to the present inventors, however, it is believed that they are related to the ratio among the raw materials in the suspension. In other words, when the aforementioned raw material charging coefficient (T) among the ratios of the raw material components in the suspension is larger than 2.5, the generated calcium sodium silicate becomes a 12 Å type or 13 Å type mica-shaped calcium sodium silicate containing amorphous silica.

The conditions for generating pectolite, 12 Å type 13 Å type or their mixture cannot be determined univocally. Although the conditions vary depending on the types of raw materials, temperature, etc., in general, when the value of T is close to 1.2 and U has a large value, the 13 Å type is easy to obtain. Also, it is easier to obtain the 13 Å type when quartz sand is used as the silica raw material instead of sodium silicate. If the hydrothermal reaction is carried out at a low temperature, the 13 Å type is easy to obtain. The fibrous pectolite is easy to obtain when T has a small value, U has a large value, and the reaction temperature is high. When pectolite is generated, there are only peaks of pectolite in the X-ray pattern. However, the result of the chemical analysis shows that the content of CaO is less and the contents of Na_2O and SiO_2 are more than in the standard composition of pectolite. In observation under a microscope, only fibrous crystals are observed. At present, it is still unclear in what form pectolite is mixed with Na_2O and SiO_2. Since the reason for this phenomenon is not yet clear, it is preferred to carry out a small-scale experiment before generating the targeted product.

Although the conditions for generating the targeted product of the present invention cannot be determined univocally, the general tendencies can be explained in more detail as follows. Since the type of raw material used for the silicon dioxide component and the temperature of the hydrothermal reaction have the most significant influence on the manufacturing conditions of the targeted product, the targeted product can be determined by appropriately selecting the aforementioned two conditions.

For example, when a compound with a low water solubility, such as said hydrous silicic acid or quartz, is used as the raw material for the silicon dioxide component, with the temperature of the hydrothermal reaction taken as t(°C), pectolite will be manufactured in most cases if the raw material charging coefficient (T) is in the range of 1.2-(0.006t + 0.15), and the alkalinity coefficient (U) is larger than 0.01. If the raw material charging coefficient (T) is in the aforementioned range and the alkalinity coefficient (U) is smaller than 0.01, the 12 Å type will be manufactured in most cases. Also, if the raw material charging coefficient (T) is in the range of (0.006t + 0.15)-(0.008t + 0.6) and the alkalinity coefficient (U) is in the range of (0.00008t - 0.008)-0.04, the 13 Å type will be manufactured in most cases. If the raw material charging coefficient (T) is in the aforementioned range and the alkalinity coefficient (U) is in the range of 0.01-(0.00008t - 0.008), the 12 Å type will be manufactured in most cases. In addition, if the raw material charging coefficient (T) is in the range of (0.008t + 0.6)-3.0 and the alkalinity coefficient (U) is in the range of 0.002-0.04, a mixture of the 12 Å type and silicon dioxide may be generated.

When a water-soluble compound, such as sodium silicate or clay, is used as the raw material for the silicon dioxide component, with the temperature of the hydrothermal reaction taken as t(C), if the raw material charging coefficient (T) is in the range of 1.2-(0.00533t + 0.4)

and the alkalinity coefficient (U) is in the range of 0.01-0.04, pectolite will be manufactured in most cases. If the raw material charging coefficient (T) is in the aforementioned range and the alkalinity coefficient (U) is smaller than 0.01, the 12 Å type will be manufactured in most cases. If the raw material charging coefficient (T) is in the range of $(0.00533t + 0.4)-(0.008t + 0.8)$ and the alkalinity coefficient (U) is in the range of $0.002-(0.0002t - 0.025)$, the 12 Å type will be manufactured in most cases. If the raw material charging coefficient is in the aforementioned range and the alkalinity coefficient (U) is in the range of $(0.0002t - 0.025)-0.04$, the 13 Å type will be manufactured in most cases. Also, if the raw material charging coefficient (T) is in the range of $(0.008t + 0.8)-3.0$ and the alkalinity coefficient is in the range of 0.002-0.04, a mixture of the 12 Å type and silicon dioxide might be generated.

Consequently, the essential conditions should be determined from the aforementioned ranges corresponding to the targeted product.

As the reaction for generating the calcium sodium silicate of the present invention, a hydrothermal reaction must be carried out under pressurization for the aforementioned suspension containing the silicon dioxide component, calcium component and sodium component. There is no special limitation on the temperature of the hydrothermal reaction as long as calcium sodium silicate can be generated. In industry, however, the temperature is usually set in the range of 150-250°C. If the temperature is too low, it will take a long time to generate the calcium sodium silicate. On the other hand, if the temperature is too high, an expensive device is needed as far as the pressure resistance of the reaction container is concerned. The vapor pressure at the aforementioned temperature is usually high enough to accommodate the reaction pressure. There is no need to use an inert gas for special pressurization. In general, the calcium sodium silicate of the present invention can be obtained by carrying out the reaction at the aforementioned temperature in a sealed container, such as an autoclave. In the present invention, the reaction time cannot be determined univocally because it varies depending on the types of raw materials, reaction conditions, etc. However, the reaction time is usually in the range of 5-40 h. In most cases, the reaction time is determined by the raw material used for the silicon dioxide component. When hydrous silicic acid, clay or sodium silicate is used, the reaction is usually completed in 20 h. Also, it is preferred to stir the suspension during the reaction for uniform dispersion and to prevent solidification.

As described above, the calcium sodium silicate of the present invention obtained as a result of the aforementioned hydrothermal reaction is in various forms depending on the raw material composition. The calcium sodium silicate obtained as a result of the hydrothermal reaction is usually separated by being filtered from the reaction system. If necessary, the obtained calcium sodium silicate is rinsed and dried to obtain the final product. Also, crystalline calcium sodium silicate can be obtained by extracting amorphous silica from the calcium sodium

silicate after it is filtered or dried. There is no special limitation on the means used for extracting the amorphous silica, and any conventional means can be used. For example, the calcium sodium silicate can be brought in contact with an alkali hydroxide with a normality of 0.2-1.0. However, since the sodium constituting part of the calcium sodium silicate hydrate other than pectolite has ion exchangeability, an ion-exchanged calcium alkali silicate will be obtained depending on the type of alkali of the aforementioned alkali hydroxide. Consequently, it is usually preferred to use sodium hydroxide as long as there is no special request.

As can be seen from the practical examples to be explained later, the filtrate obtained by filtering the aforementioned reaction product contains almost no calcium component. However, most of the silicon dioxide component and the sodium component used as the raw materials in excess amounts is contained in the form of sodium silicate. Consequently, some or all of the filtrate can be circulated in the reaction system and used as the raw material in the present invention. In general, when calcium hydroxide or calcium oxide is used as the raw material for the calcium component in the present invention, the filtrate can be circulated directly in the reaction system because there is no by-product generated along with generation of the calcium sodium silicate. As described above, however, a sodium salt is formed as a by-product when calcium chloride, calcium nitrate or calcium sulfate is used as the raw material. If the aforementioned filtrate is directly circulated in the reaction system when a sodium salt is formed as a by-product by the reaction, the by-produced sodium salt will accumulate and will be deposited corresponding to the solubility. Therefore, when a sodium salt is by-produced by the reaction, it is preferred to circulate the filtrate as the raw material after the sodium salt is removed from some or all of the filtrate. There is no special limitation on the means used for eliminating the sodium salt from the filtrate, and any conventional means can be used. For example, it is possible to use the method that filters out an essential amount of the by-produced sodium salt by cooling the filtrate to a temperature lower than that corresponding to the solubility of the sodium salt.

For the unreacted component silicon dioxide and sodium component in the aforementioned filtrate, as can be seen from the aforementioned general formula of the calcium sodium silicate, in most cases, more silicon dioxide component than sodium component is consumed in the reaction. Consequently, the ratio among the raw material components in the filtrate is usually different from that in the suspension. In this case, it is necessary to adjust the ratio among the raw materials by adding new raw materials. In general, it is preferred to add hydrous silicic acid or clay to the filtrate. In particular, when sodium silicate is used as the silicon dioxide component and sodium component, the means for adjusting the molar ratio SiO_2 Na_2O of the filtrate by adding hydrous silicic acid or clay to the filtrate can be used effectively in industry.

The calcium sodium silicate hydrate obtained in the present invention can be used in a wide range of application fields depending on its type. For example, the fibrous pectolite can be used for construction materials, noncombustible materials and various types of reinforcing materials as a substitute for asbestos. In addition, the novel 12 Å type and 13 Å type calcium sodium silicate hydrates can be used as novel inorganic ion exchangers because they have ion exchangeabilities of about 1.6-2.1 and 3.5-4.0 milliequivalents/g, respectively.

In the following, this invention will be explained in more detail with reference to practical examples. The present invention, however, is not limited to these practical examples.

Practical Example 1

100 cc of an aqueous solution of sodium silicate with a concentration of 1.75 mol/l (molar ratio of SiO_2/Na_2O: 2.03) as Na_2O and 100 cc of slaked lime slurry with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (B) was 1.6 and the alkalinity coefficient (U) calculated from said equation (D) was 0.015. The slurry was placed and sealed in an autoclave (with a volume of 300 ml), then the reaction was carried out at 175°C for 20 h while the slurry was stirred with electromagnetic stirring blades. After the end of the reaction, the reaction product was removed from the autoclave, filtered, rinsed with 100 cc of ion-exchanged water for three times, and dried at 100°C for 8 h.

The yield of the dried reaction product was 9.5 g. The results of analyzing the reaction product based on JIS R 3101 showed 11.1% of Na_2O, 14.6% of CaO, 64.7% of SiO_2 and 9.5% of H_2O. Therefore, the reaction product can be represented by:
$2.76Na_2O \cdot 4CaO \cdot 16.5SiO_2 \cdot 8.14H_2O$. When 1 g of the reaction product was heated in a 0.5N NaOH aqueous solution at 80°C for 1 h, almost none of the reaction product was dissolved in the solution. In this way, it was confirmed that the reaction product did not contain amorphous silica or other impurities. Also, when the reaction product was examined under an electron microscope at 1000X magnification (JSM-50A (trade name), product of JEOL Ltd.) and photographed, the picture shown in Figure 1 was obtained. As can be seen from Figure 1, the reaction product is a mica-like compound that almost has a square shape. The length of each side is about 20 μ, and the thickness is 0.1 μ or smaller. The powder of the reaction product was subjected to X-ray diffraction analysis performed using an X-ray diffractometer (Rotaflex pl 200 (trade name), product of Rigaku Denki K.K.) and $CuK\alpha$ with 2θ set in the range of 5-50, obtaining the X-ray diffraction pattern diagram shown in Figure 2. Novel crystals that have not been reported so far are confirmed from the diffraction pattern diagram. The diagram also shows strong diffraction lines at spacing d(Å) 13.4, 6.7, 3.5, 3.3, 3.1, 3.0 and 2.9.

The results of analyzing the filtrate obtained by filtering the aforementioned reaction product confirmed the presence of sodium silicate but showed almost no calcium component.

Practical Example 2

100 cc of an aqueous solution of sodium silicate with a concentration of 1.75 mol/l (molar ratio of SiO_2/Na_2O: 2.31) as Na_2O and 100 cc of slaked lime slurry with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (B) was 1.8 and the alkalinity coefficient (U) calculated from said equation (D) was 0.015. The slurry was reacted in the same way as described in Practical Example 1 at 225°C for 20 h. The yield of the dried reaction product was 8.7 g.

The values of the chemical analysis were 6.1% of Na_2O, 16.1% of CaO, 63.1% of SiO_2 and 14.6% of H_2O. Therefore, the reaction product can be represented by $1.36Na_2O \cdot 4CaO \cdot 15SiO_2 \cdot 11.24H_2O$. When the reaction product was treated in a 0.5N NaOH aqueous solution at 80°C for 1 h, almost none of the reaction product was eluted. In this way, it was confirmed that the reaction product did not contain amorphous silica or other impurities. The 1000X photograph taken by an electron microscope is shown in Figure 3. The reaction product is a mica-like compound with the length of each side of about 30 μ and the thickness of 0.1 μ or smaller. The X-ray diffraction pattern diagram of the powder of the reaction product is shown in Figure 4. Novel crystals that have not been reported so far are confirmed from the diffraction pattern diagram. The diagram also shows strong diffraction lines at spacing d(Å) = 12.0, 6.0, 3.4 and 3.0.

Practical Example 3

100 cc of an aqueous solution of sodium silicate with a concentration of 1.53 mol/l (molar ratio of SiO_2/Na_2O: 3.14) and 100 cc of slaked lime slurry with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (B) was 2.7 and the alkalinity coefficient (U) calculated from said equation (D) was 0.013. The slurry was placed and sealed in an autoclave and reacted at 175°C for 20 h. The same processing as described in Practical Example 1 was then carried out to obtain a dried reaction product. The results of the chemical analysis of the reaction product were 4.7% of Na_2O, 12.6% of CaO, 70.6% of SiO_2, Al_2O_3 and 12.0% of H_2O. The reaction product was treated in a 0.5N NaOH aqueous solution at 80°C for 1 h, followed by rinsing and drying. The results of the chemical analysis of the reaction product

treated with the alkali were 5.8% of Na_2O, 15.4% of CaO, 64.3% of SiO_2, Al_2O_3 and 14.5% of H_2O.

Depending on the results obtained by performing the aforementioned alumina correction for the aforementioned analytical data, it is clear that the calcium sodium silicate hydrate can be represented as $1.36Na_2O \cdot 4CaO \cdot 15.6SiO_2 \cdot 11.64H_2O$ after the alkali treatment and as $(1.36Na_2O \cdot 4CaO \cdot 15.6SiO_2 \cdot 11.64H_2O)(5.3SiO_2 \cdot 0.2H_2O)$ before the alkali treatment. Both of the X-ray diffraction pattern diagrams before and after the alkali treatment are almost the same as that shown in Figure 4. When the reaction product is observed with an electron microscope, it is confirmed that the reaction product barely changes before and after the alkali treatment. The reaction product is a mica-like compound with the length of each side of about 2 μ.

Practical Example 4

100 cc of an aqueous solution of sodium silicate with a concentration of 1.73 mol/l (molar ratio of SiO_2/Na_2O: 1.66) as Na_2O and 100 cc of slaked lime slurry with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (B) was 1.2 and the alkalinity coefficient (U) calculated from said equation (D) was 0.015. After the slurry was placed and sealed in an autoclave, it was reacted at 200°C for 20 h. The reaction product was processed in the same way as described in Practical Example 1 to obtain a dried reaction product. The yield was 4.15 g.

The results of the chemical analysis were 12.1% of Na_2O, 23.4% of CaO, 56.1% of SiO_2 and 8.4% of H_2O. The 100X photograph taken by an electron microscope is shown in Figure 5. The reaction product consists of fibrous crystals with a side length of about 100 μ.

The X-ray diffraction pattern diagram is shown in Figure 6. A well-known pectolite is confirmed from the diffraction pattern diagram.

Practical Example 5

Sodium silicate and slaked lime were mixed in 200 cc of water. The reaction was then carried out at different temperatures for 20 h in the same way as described in Practical Example 1, followed by filtering, rinsing and drying to obtain a reaction product. The results of analyzing the powder of the dried reaction product by means of X-ray diffraction are listed in Table 1. The pectolites listed in the table are in fibrous form, and mica-like compounds are also observed with a microscope.

Table 1.

Key: 1   Charging No.
2   Composition of the suspension
3   Moles
4   Raw material charging coefficient (T)
5   Alkalinity coefficient (U)
6   Reaction temperature
7   Yield (g)
8   X-ray results
9   Length of one side
10   Pectolite

Practical Example 6

A slurry was prepared by adding sodium hydroxide and slaked lime to 190 cc of water in the molar amounts of Na_2O and CaO listed in Table II, respectively. The raw material for the silica component listed in Table II was then added to obtain another slurry. The obtained slurry was placed and sealed in an autoclave and reacted at 175° C for 20 h. The reaction product was then processed in the same way as described in Practical Example 1 to obtain a dried reaction product. The results are listed in Table II. Tokusil [transliteration] Gu (trade name) was used as the hydrous silicic acid. The clay used in this case was Beffu [transliteration] clay with a size that allows complete passage through a 325-mesh screen. The quartz used in this case had a size that allows complete passage through a 325-mesh screen. Also, all of the results of X-ray

diffraction are similar to those shown in Figure 2. All of the reaction products are shaped like mica.

Table II.

⑥		1	2	3	4
⑤		① ④水珪酸	③④水珪酸	④粘土	⑤石英
⑦ SiO₂ (モル)⑦		0.372	0.464	0.372	0.372
	Na₂O (モル)⑧	0.175	0.342	0.175	0.175
	CaO (モル)⑨	0.025	0.025	0.025	0.025
原料仕込み係数 (T)⑧		1.7	1.7	1.7	1.7
アルカリ度係数 (U)⑨		0.015	0.050	0.015	0.015
収 量 (g)⑩		9.5	9.6	9.6	9.6
X線回折結果⑪		1 5 Å	1 5 Å	1 5 Å	1 2 Å
結晶最大長さ⑫		3 0 μ	3 0 μ	4 0 μ	4 0 μ

Key: 1   Type of SiO₂ raw material
        2   Hydrous silicic acid
        3   Hydrous silicic acid
        4   Clay
        5   Quartz
        6   Composition of the suspension
        7   Moles
        8   Raw material charging coefficient (T)
        9   Alkalinity coefficient (U)
        10   Yield (g)
        11   X-ray diffraction results
        12   Maximum crystal length

Practical Example 7

1.4 g of calcium oxide were pulverized to a size that allowed passage through a 100-mesh screen, then added to 100 cc of water. The reaction was carried out in the same way as described in Practical Example 1 except that the aforementioned slurry was used instead of the 0.25 mol l slaked lime slurry used in Practical Example 1. The results of the X-ray diffraction of the powder of the reaction product are the same as those shown in Figure 2. The yield was 9.6 g. Mica-like crystals with a side length of 30 μ were observed with an electron microscope.

Practical Example 8

1.4 g of calcium oxide were pulverized to a size that allowed passage through a 100-mesh screen and added to 100 cc of water. The reaction was carried out in the same way as described in Practical Example 2 except that the aforementioned slurry was used instead of the 0.25 mol/l slaked lime slurry used in Practical Example 2. The results of the X-ray diffraction of the reaction product are the same as those shown in Figure 4. The yield was 8.6 g. Mica-like crystals with a side length of about 30 μ were observed with an electron microscope.

Practical Example 9

100 cc of an aqueous solution of sodium silicate with a concentration of 2.0 mol/l (molar ratio of SiO_2/Na_2O: 1.78) and 100 cc of an aqueous solution of calcium chloride with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (A) was 1.60 and the alkalinity coefficient (U) calculated from said equation (C) was 0.015. Although a white precipitate was generated during mixing, the slurry was directly placed and sealed in an autoclave and reacted at 200°C for 20 h. The reaction product was then processed in the same way as described in Practical Example 1, obtaining 9.4 g of dried reaction product. After observation under an electron microscope, it was found that the reaction product was a mica-like compound with a side length of 50 μ. The results of the chemical analysis indicated that the reaction product can be represented by $2.72Na_2O \cdot 4CaO \cdot 15.6SiO_2 \cdot 8.28H_2O$. The results of the X-ray diffraction are the same as those shown in Figure 2.

Practical Example 10

100 cc of an aqueous solution of sodium silicate with a concentration of 2.0 mol/l (molar ratio of $SiO_2 Na_2O$: 2.02) as Na_2O and 100 cc of an aqueous solution of calcium chloride with a concentration of 0.25 mol/l were mixed at 25°C under atmospheric pressure. In this case, the raw material charging coefficient (T) calculated from said equation (A) was 1.8 and the alkalinity coefficient (U) calculated from said equation (C) was 0.015. Although a white precipitate was generated during mixing, the slurry was directly placed and sealed in an autoclave and reacted at 200°C for 20 h. The reaction product was then processed in the same way as described in Practical Example 1, obtaining 8.7 g of dried reaction product. The results of the chemical analysis indicated that the reaction product can be represented by $14Na_2O \cdot 4CaO \cdot 16.2SiO_2 \cdot 10.5H_2O$. The results of the X-ray diffraction are almost the same as those shown in Figure 4. After observation under an electron microscope, it was found that the reaction product consisted of fibrous crystals with a side length of about 30 μ.

Practical Example 11

The reaction was carried out in the same way as described in Practical Example 9 except that an aqueous solution of calcium nitrate and an aqueous solution of calcium sulfate were used instead of the aqueous solution of calcium hydroxide used in Practical Example 9. The yields were 9.6 g and 9.7 g, respectively. The results of X-ray diffraction of both of the reaction products are the same as those shown in Figure 2. It is confirmed that the reaction products are the same as the crystals obtained in Practical Example 1. After observation under an electron microscope, it was confirmed that the reaction products are mica-like crystals with the length of one side of about 30 μ and 50 μ, respectively.

Practical Example 12

The reaction was carried out in the same way as described in Practical Example 10 except that an aqueous solution of calcium nitrate and an aqueous solution of calcium sulfate were used instead of the aqueous solution of calcium hydroxide used in Practical Example 10. The yields were 8.8 g and 8.9 g, respectively. The results of X-ray diffraction of both of the reaction products are almost the same as those shown in Figure 4. It is confirmed that the reaction products are the same as the crystals obtained in Practical Example 2. After observation under an electron microscope, it is confirmed that the reaction products are mica-like crystals with the length of one side of about 20 μ and 30 μ, respectively.

4. Brief description of the drawings

Figures 1, 3 and 5 are diagrams illustrating the enlarged pictures taken by a scanning electron microscope of the calcium sodium silicate hydrate manufactured according to the present invention. Figures 2, 4 and 6 are diagrams illustrating the X-ray diffraction patterns of the calcium sodium silicate hydrate manufactured according to the present invention.
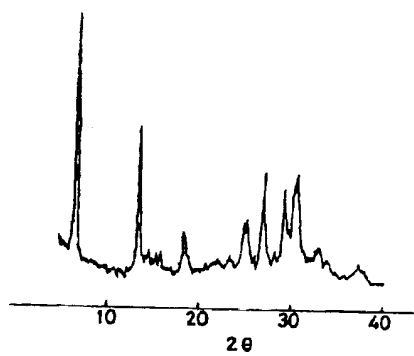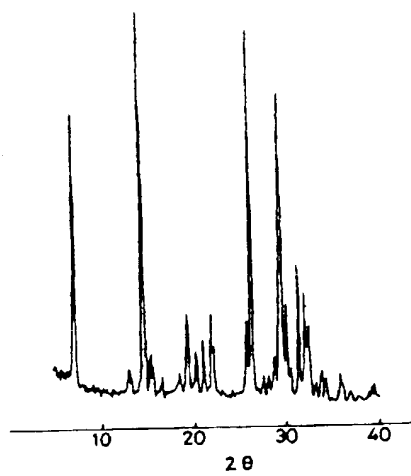
Figure 1

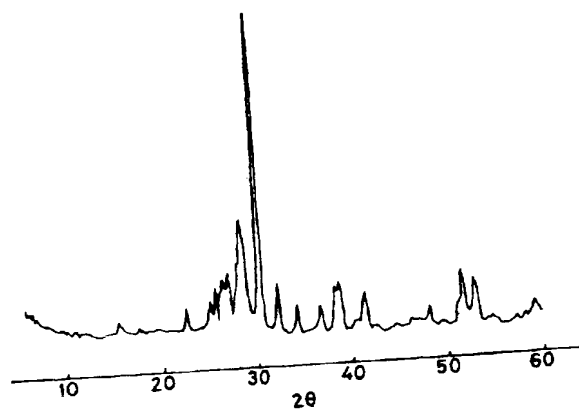10   20   30   40

2 θ

Figure 2

Figure 3

2 θ

Figure 4

Figure 5

Figure 6